

Scientific Report
Dec. 2014– Dec. 2015

New metal complexes with metal-chalcogen bonds - potential precursors for electronic materials. code PN-II-ID-PCE_2011-3-0659

The objectives accomplished during this period were as followings, according to the proposed research project:

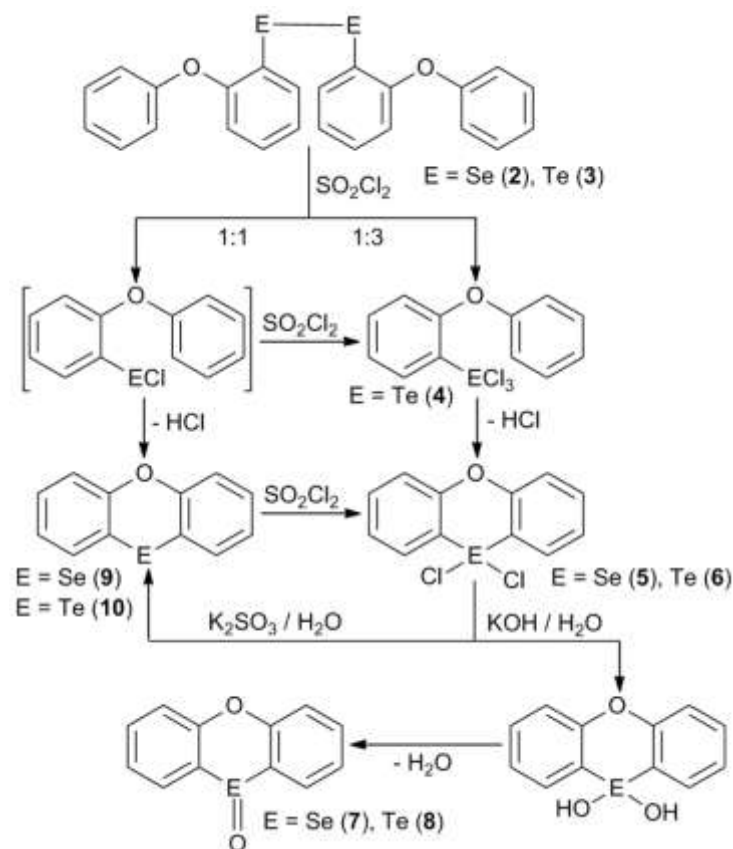
- Studies regarding the reactivity of several new organo-chalcogen ligands.
- Synthesis and structural characterization of several new organometallic (Sb, Bi or Sn) compounds with organochalcogen- or alkoxo ligands.
- New organometallic compounds of main group metals (Sb, Bi or Sn) with organo-chalcogen ligands.
- New complexes of *d* metals with organo-chalcogen (Se, Te) ligands. Synthesis and structural characterization.
- Thermal behavior of the new precursors and preliminary studies regarding their vapor deposition.
- Final characterization of several compounds obtained before 2015.
- Dissemination of the results, manuscripts' preparation.

The new compounds were characterized by multinuclear NMR (^1H , ^{13}C , ^{31}P , ^{77}Se , ^{125}Te , as appropriate) and mass spectrometry. Part of them were characterized by IR spectroscopy, powder or single-crystal X-ray diffraction. 2D NMR experiments (COSY, HSQC, HMBC) were used to assign the resonances for several of the investigated species and the dynamic behavior in solution of some compounds was studied by variable temperature NMR. Majority of the reactions were performed under argon atmosphere, using dry and freshly distilled solvents, in order to avoid the decomposition either of the starting materials or the products by aerial oxidation or hydrolysis.

1. Studies regarding the reactivity of several new organo-chalcogen ligands

The oxidation of the diorganodichalcogenides of type $[(\text{C}_6\text{H}_5)\text{O}(\text{C}_6\text{H}_4)]_2\text{E}_2$ [$\text{E} = \text{S}$ (**1**), Se (**2**), Te (**3**)] with SO_2Cl_2 in a 1:1 molar ratio, in anhydrous conditions led to the formation of

$[(\text{C}_6\text{H}_5)\text{O}(\text{C}_6\text{H}_4)]\text{TeCl}_3$ (**4**) and respectively the cyclic species $[(\text{C}_6\text{H}_5)\text{O}(\text{C}_6\text{H}_4)]\text{SeCl}_2$ (**5**) (Scheme 1), both of them containing the chalcogen in the oxidation state +4. In reaction with aqueous KOH solutions, the two species led to a mixture of phenoxachalcogenine and phenoxachalcogenine oxide, according to Scheme 1. When the reaction of $[(\text{C}_6\text{H}_5)\text{O}(\text{C}_6\text{H}_4)]_2\text{S}_2$ with SO_2Cl_2 was performed, the cyclic $[(\text{C}_6\text{H}_5)\text{O}(\text{C}_6\text{H}_4)]\text{S}$ was identified by NMR in mixture with other products and it could not be separated.



Scheme 1.

^{77}Se and respectively ^{125}Te NMR studies were employed in order to understand the respective oxidation processes. The chemical shifts observed in these spectra are relevant for the contained chalcogens in the respective oxidation state.

Compounds **4**, **5** and **7** in Scheme 1 were investigated by single-crystal X-ray diffraction.

In the crystal of compound **4** dimeric associations were observed (Figure 1), formed by $\text{Te}\cdots\text{Cl}$ intermolecular interactions ($\text{Te1}\cdots\text{Cl3}'$ 3.584(2) Å vs. $\Sigma r_{\text{vdW}}(\text{Te}, \text{Cl})$ 4.00 Å). In addition, π interactions ($\text{Te}\cdots\text{C}_g$ 3.833 Å) contribute to the stabilization of the dimeric structure.

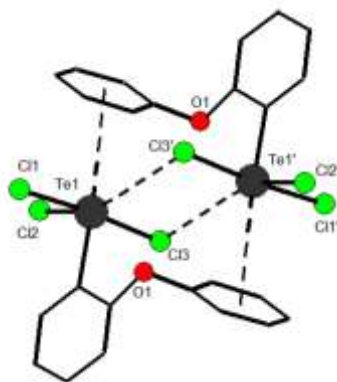


Figure 1. Dimeric association in compound **4**.

In compound **5** the molecules are associated in polymeric chains by hydrogen bonding ($\text{Cl1}\cdots\text{H11}'$ 2.76 Å, vs. $\Sigma r_{\text{vdW}}(\text{Cl},\text{H})$ 3.01 Å) (Figure 2).

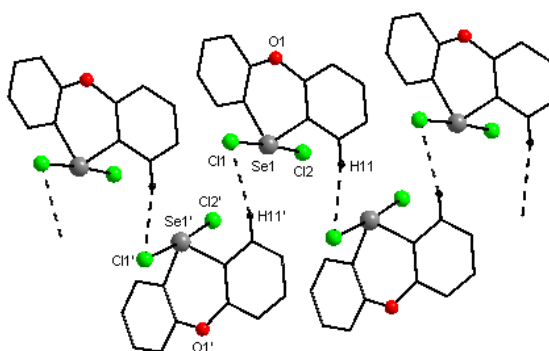


Figure 2. Polymeric association in compound **5**.

The redox behavior of the diorganodichalcogenides **2** and **3** was investigated by cyclic voltammetry. The voltamograms suggested the primary formation of phenoxachalcogenine, followed by oxidation to the corresponding phenoxachalcogenine dichloride.

2. Organometallic compounds of group 14 (Sn) and 15 (Sb, Bi) with organochalcogen ligands.

2.1. Hypervalent organobismuth(III) compounds with ligands of type $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{E}]$ (E = S, Se)

The compound $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiOSO}_2\text{CF}_3$ was prepared by reacting $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiBr}$ with $\text{AgOSO}_2\text{CF}_3$ in a 1:1 molar ratio. The spectroscopic data (^1H , ^{13}C , ^{19}F

RMN, APCI+ MS and IR) revealed the formation of the metal complex and a bidentate coordination of the OSO_2CF_3 ligand. The CH_2 protons are not equivalent and they give an AB spin system in the ^1H NMR spectrum, thus suggesting an intramolecular $\text{S} \rightarrow \text{Bi}$ coordination in solution. The IR spectra contain characteristic bands for the $\nu_{\text{as}}\text{SO}_2$, $\nu_{\text{s}}\text{SO}_2$ and νSO vibrations, thus suggesting an anisobidentate coordination of the OSO_2CF_3 ligand. The molecular structure of the compound, determined by single-crystal X-ray diffraction has shown the intramolecular $\text{S} \rightarrow \text{Bi}$ coordination in solid state, thus resulting in a hypervalent *12-Bi-5* species. The molecules are associated in a 2D supramolecular network by $\pi \text{C}_g \cdots \text{Bi}$ and respectively $\text{O} \cdots \text{H}$ intermolecular interactions (Figure 3).

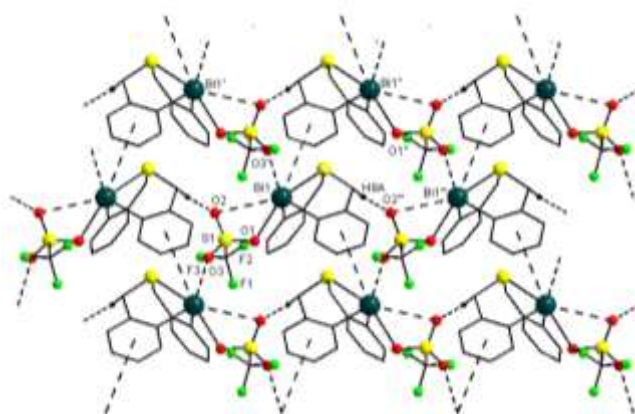


Figure 3. 2D network in $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiOSO}_2\text{CF}_3$

An experimental and theoretical study upon the structural data of several compounds of type $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ONO}_2, \text{OSO}_2\text{CF}_3$) revealed that the $\text{S} \rightarrow \text{Bi}$ interatomic distance decrease in the order $\text{Cl}, \text{Br}, \text{I} > \text{ONO}_2 > \text{OSO}_2\text{CF}_3$, with approx. the same strength in the halides (approx. 2.84 Å). DFT calculations upon the same series of compounds revealed the order $[(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiOSO}_2\text{CF}_3 > [(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiONO}_2 > [(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiCl} > [(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiBr} > [(\text{C}_6\text{H}_4\text{CH}_2)_2\text{S}]\text{BiI}$ for the strength of the $\text{S} \rightarrow \text{Bi}$ interaction, in accordance with the variation of the ionic character of the $\text{Bi}-\text{X}$ bond.

2.2. Organotin(IV) compounds with dithiocarbamate ligands

Several new organotin(IV) dithiocarbamates were prepared. The ^{119}Sn NMR resonance appears as a singlet in these species, by contrast with the compound $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})_2$ for which a triplet resonance was observed, due to the $^{15}\text{N} - ^{119}\text{Sn}$ coupling.

The single-crystal X-ray diffraction studies revealed an ionic structure of the obtained compounds, with an octahedral coordination geometry about tin in the cation $[\{2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2\text{Sn}(\text{S}_2\text{CNMe}_2)]^+$.

2.3. Ionic species of type $[\text{Ph}_3\text{Te}]^+[\text{R}_2\text{SbX}_4]^-$

Ionic species containing the triphenyltelluronium cation and organoantimony(V) anions of type R_2SbX_4^- ($\text{R} = \text{Ph}, 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$) were prepared by the reaction between Ph_3TeCl or $\text{Ph}_3\text{Te}(\text{XCN})$ ($\text{X} = \text{S}, \text{Se}$) with R_2SbX_3 halides in a 1:1 molar ratio. The new species have a molar conductivity corresponding to 1:1 electrolytes, and the mass spectra are also in accordance with the existence of the two ions in solution.

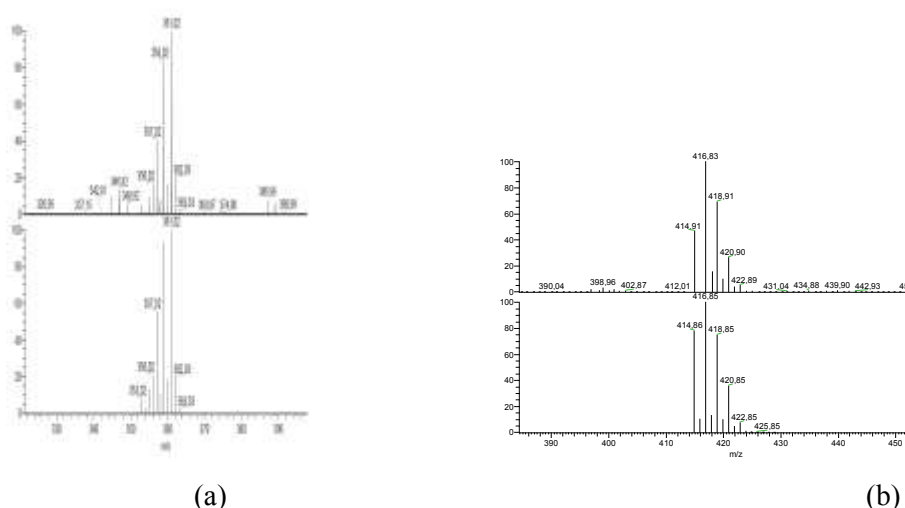


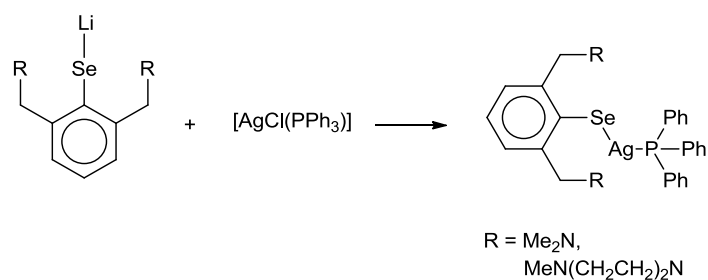
Figure 4. Experimental (above) and calculated (below) APCI+ MS (a) and ESI- MS (b) spectra of $[\text{Ph}_3\text{Te}]^+[\text{Ph}_2\text{SbCl}_4]^-$.

In Figure 4 are depicted the APCI+ MS and respectively ESI- MS spectra for the compound $[\text{Ph}_3\text{Te}]^+[\text{Ph}_2\text{SbCl}_4]^-$. The experiments regarding the thermal behavior of these species are in progress.

3. New *d* metal complexes with organochalcogen ligands

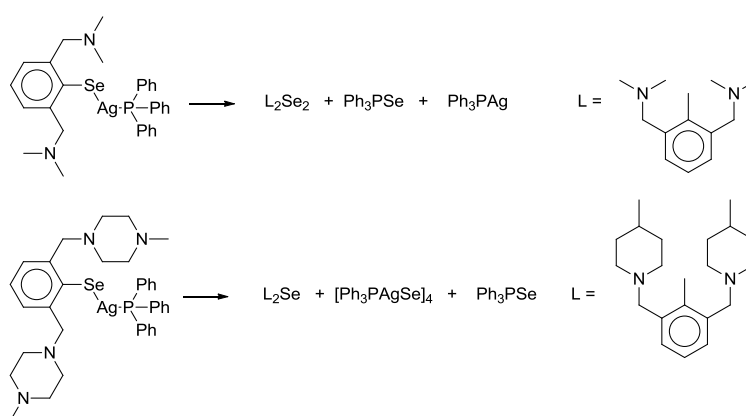
3.1. Group 11 metal complexes with organochalcogen ligands with two pendant arms

As a continuation of our studies related to the group 11 metal complexes with ligands of type $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_3]\text{E}^-$ ($\text{E} = \text{S}, \text{Se}$), we prepared several silver(I) complexes, according to Scheme 2.



Scheme 2.

The NMR studies suggested the decomposition of these species in solution, resulting in Ph_3PSe and the starting Ph_3PAg . We could also isolate and structurally characterize the tetrameric species $(\text{Ph}_3\text{PAgSe})_4$ formed also during the decomposition process (Scheme 3):



Scheme 3

The crystal and molecular structure of the tetrameric species was determined by single-crystal X-ray diffraction and it is displayed in Figure 5. The compound has a cubane-like structure, with the silver and selenium atoms occupying alternatively the corners of the cubane.

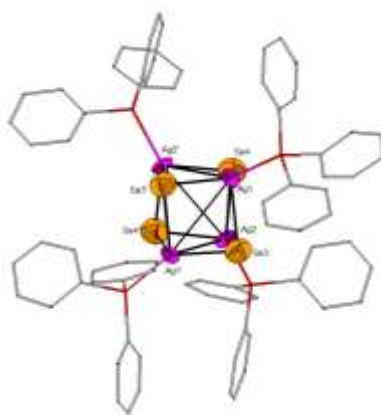


Figure 4. Tetrameric association in $(\text{Ph}_3\text{PAgSe})_4$

3.2. Au and Ag complexes with macrocyclic ligands containing N/ S/ Se donor atoms

During our studies, we obtained a 28-membered macrocyclic ligand which was subsequently used for the preparation of group 11 metal complexes. The ^1H NMR spectrum of the ligand, as well as those of the silver and respectively gold complexes are in accordance with the expected structure and a 1:1 stoichiometry. For one of the Ag(I) complexes the molecular structure was determined by single-crystal X-ray diffraction.

3.3. Co(II) complexes with ligands with XPNSO skeleton

The studies related to the cobalt(II) complexes with ligands of type $(\text{XPR}_2)(\text{O}_2\text{SR})\text{NH}$ [$\text{X} = \text{S}$; $\text{R} = \text{Ph}$; $\text{R}' = \text{Me}$, Ph , $\text{C}_6\text{H}_4\text{CH}_3\text{-4}$; $\text{X} = \text{O}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Ph}$, $\text{R} = \text{OEt}$, $\text{R}' = \text{C}_6\text{H}_4\text{CH}_3\text{-4}$] were completed during this stage. For one of the compounds a dinuclear structure was determined by single-crystal X-ray diffraction, with the ligands acting differently, *e.g.* one of them bridging the two metal centers as a *S,O,O*-bimetallic triconnectiv moiety, while the other two acting as terminal *S,O*-monometallic biconnectiv units. The oxidation process of Co(II) in $\text{Co}[(\text{SPPH}_2)(\text{O}_2\text{SMe})\text{N}]_2$ to Co(III) in $\text{Co}(\text{OH})[(\text{SPPH}_2)(\text{O}_2\text{SMe})\text{N}]_2$, observed during the recrystallization process, was investigated by cyclic voltametry.

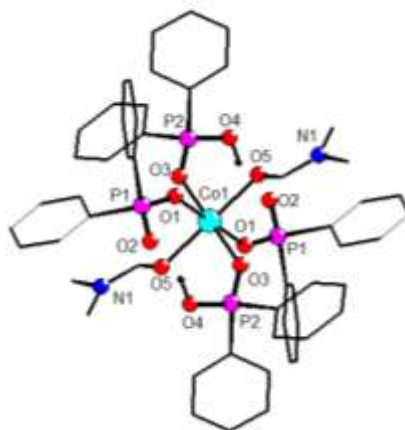


Figure 6. Molecular structure of $\text{Co}[(\text{O}_2\text{PPh}_2)(\text{HO}_2\text{PPh}_2)(\text{dmfa})]_2$

In dimethylformamide the complex $\text{Co}[(\text{OPPh}_2)(\text{O}_2\text{SOPh})\text{N}]_2$ decomposed leading to the adduct $\text{Co}[(\text{O}_2\text{PPh}_2)(\text{HO}_2\text{PPh}_2)(\text{dmfa})]_2$, with an octahedral environment about cobalt (Figure 6).

4. Thermal behavior of the synthesized precursors

Several compounds were investigated by thermogravimetric analysis, in order to establish the decomposition way by increasing the temperature. The Sn(IV) species [$\{2\text{-}$

$(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_4\text{Sn}(\text{S}_2\text{CNR}_2)]^+\text{SCN}^-$ (R = Me, Et) were stable up to approx. 180°C, value above which they decompose over a narrow temperature range (180 – 272°C and respectively 178 – 294°C, when SnS is formed. The powder X-ray diffraction and the EDX studies upon the obtained powders are in progress. For the ionic species $[\text{Ph}_3\text{Te}]^+[\text{Ph}_2\text{SbCl}_4]^-$ the thermogravimetric analysis suggests a more complex process in which labile intermediates are formed.

5. Finalizing step of several studies developed in 2012-2014

Several studies regarding the characterization of the new species obtained before 2015 were completed. For some selected processes additional evidences were brought by DFT calculations. The obtained results were the subject of several papers or were communicated to different events, as appears below.

RESULTS

Published papers, results obtained in 2014

1. Diorganodichalcogenides and their intramolecular cyclization reactions.
A. Pöllnitz, A. Silvestru,
Tetrahedron, **2015**, 71, 2914-2921, doi.org/10.1016/j.tet.2015.03.058
2. New triphenyltelluronium salts of organophosphorus ligands.
N. Chiorean, D. Margineanu, A. Silvestru
Rev. Roum. Chim., **2014**, 59(11-12), 953-958.
3. Spectroscopic and thermal studies on the iron(III) mercapto-thiadiazol-thiosuccinate precursor for iron(III) oxides
M. M. Venter, F. Goga, V. N. Bercean, M. Nasui, G. Borodi,
Rev. Roum. Chim., **2014**, 59(11-12), 989-996.

Published (or in preparation) papers, results obtained in 2015

1. Cobalt(II) complexes of organophosphorus ligands with XPNSO skeleton (X = O, S). Solid state structure and solution behavior.
Eleonora Denes, Alpar Pöllnitz, Florentina Cziple, Mihaela Vlassa and Anca Silvestru,
Inorganica Chimica Acta, in press.
2. Heterocyclic bismuth(III) compounds with transannular S→Bi interactions. An experimental and theoretical approach.
Ana Toma, Ciprian I. Raț, Anca Silvestru, Tobias Rüffer, Heinrich Lang and Michael Mehring
manuscript submitted for publication, *Journal of Organometallic Chemistry*, in press.

3. Bis(2-phenoxyphenyl)dichalcogenides and their chemical reactivity.
Ana Maria Toma, Adrian Nicoara, Anca Silvestru, Tobias Rüffer, Heinrich Lang and Michael Mehring
Journal of Organometallic Chemistry, JORGANCHEM-S-15-00840.
4. Silver(I) complexes of a new multidentate macrocyclic ligand with N/S/Se donor atoms.
Roxana A. Popa, Anca Silvestru and Alexandra Pop
Journal of Organometallic Chemistry, sent.
5. Organoselenium compounds with (N,C,N) pincer ligands. Structure and chemical behaviour.
Alexandra Pop and Anca Silvestru
Journal of Organometallic Chemistry, in preparation.

Conferences 2015

1. From diorganodichalcogenides to heterocycles.
Anca Silvestru, *oral presentation* at TRAMECH VIII, Antalya (Turcia), Nov. 2015.
2. New multidentate macrocyclic ligands containing Se/S/N donor atoms and their late d-metal complexes,
Alexandra Pop, *poster presentation* at EuCOMC XXI International Conference on Organometallic Chemistry, Bratislava, Slovakia, July 2015.
3. New organotellurium compounds with 2-(Me₂NCH₂)C₆H₄ groups,
Denes Eleonora, *poster presentation* at 12th International Conference Students for Students, Cluj-Napoca, April 2015.

28.11.2015

Project director,

Prof. Dr. Anca Silvestru

